

CLAIMS

What is claimed is:

1. A supported chromium catalyst comprising:
 - chromium oxide,
 - a silica-containing support comprising silica selected from the group consisting of silica having:
 - (a) a pore volume of about 1.1 to about 1.8 cm³/g and a surface area of about 245 to about 375 m²/g,
 - (b) a pore volume of about 2.4 to about 3.7 cm³/g and a surface area of about 410 to about 620 m²/g, and
 - (c) a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g;
 - and,
 - an organoaluminum compound;

wherein said supported chromium catalyst is activated at about 400 to about 860°C.
2. The catalyst of claim 1 wherein said organoaluminum compound is added in situ.
3. The catalyst of claim 1 wherein said organoaluminum compound is an alkyl aluminum alkoxide compound.
4. The catalyst of claim 3 wherein said alkyl aluminum alkoxide compound is diethyl aluminum ethoxide.
5. The catalyst of claim 3 formed by the in-situ addition of said alkyl aluminum alkoxide compound.

6. The catalyst of claim 5 wherein said alkyl aluminum alkoxide compound is diethyl aluminum ethoxide.
7. The supported catalyst of claim 1 wherein said supported chromium catalyst is activated at about 600 to about 860°C.
8. The catalyst of claim 1 further comprising titanium tetraisopropoxide.
9. The catalyst of claim 1 wherein said organoaluminum compound is an alkyl aluminum compound.
10. The catalyst of claim 9 wherein said alkyl aluminum compound is selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum.
11. The catalyst of claim 9 formed by the in situ addition of said alkyl aluminum compound.
12. The catalyst of claim 11 wherein said alkyl aluminum compound is triethyl aluminum.
13. The catalyst of claim 1 wherein said silica has a pore volume of about 2.4 to about 3.7 cm³/g and a surface area of about 410 to about 620 m²/g and said organoaluminum compound is an alkyl aluminum alkoxide compound.
14. A supported chromium catalyst system comprising:
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silylchromate,
 - a silica-containing support, dehydrated at about 400 to about 860°C, comprising silica selected from the group consisting of silica having:
 - (a) a pore volume of about 1.1 to about 1.8 cm³/g and a surface area of about 245 to about 375 m²/g, (b) a pore volume of about 2.4 to about 3.7 cm³/g and a surface area of about 410 to

about 620 m²/g, and (c) a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g;

an organoaluminum compound,

formed by the process of adding said organoaluminum compound in situ.

15. The catalyst of claim 14 wherein said organoaluminum compound is an alkyl aluminum alkoxide compound.
16. The catalyst of claim 15 wherein said alkyl aluminum alkoxide compound is diethyl aluminum ethoxide.
17. The catalyst of claim 14 wherein said organoaluminum compound is an alkyl aluminum compound.
18. The catalyst of claim 17 wherein said alkyl aluminum compound is selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum.
19. A supported chromium catalyst system comprising:
 - silylchromate,³
 - a silica-containing support, dehydrated at about 400 to about 860°C, comprising silica selected from the group consisting of silica having a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g; and,⁴
 - an organoaluminum compound.
20. A supported chromium catalyst system comprising:
 - silylchromate,

a silica-containing support, dehydrated at about 400 to about 860°C, comprising silica selected from the group consisting of silica having:

(a) a pore volume of about 1.1 to about 1.8 cm³/g and a surface area of about 245 to about 375 m²/g, (b) a pore volume of about 2.4 to about 3.7 cm³/g and a surface area of about 410 to about 620 m²/g, and (c) a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g;

an organoaluminum compound selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum,

formed by the process of adding said organoaluminum compound in catalyst.

21. A supported chromium catalyst system comprising:

silylchromate,

a silica-containing support, dehydrated at about 400 to about 860°C, comprising silica selected from the group consisting of silica having:

(a) a pore volume of about 1.1 to about 1.8 cm³/g and a surface area of about 245 to about 375 m²/g, (b) a pore volume of about 2.4 to about 3.7 cm³/g and a surface area of about 410 to about 620 m²/g, and (c) a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g;

and,

triethyl boron,

formed by the process of adding said triethyl boron in situ.

22. A process for producing an ethylene polymer comprising the steps of:
contacting ethylene under polymerization conditions with a catalyst system, said catalyst system comprising chromium oxide, an alkyl aluminum, and a silica-containing support comprising silica selected from the group consisting of silica having:
(a) a pore volume of about 1.1 to about 1.8 cm³/g and a surface area of about 245 to about 375 m²/g, (b) a pore volume of about 2.4 to about 3.7 cm³/g and a surface area of about 410 to about 620 m²/g, and (c) a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g;
and,
controlling one or more of catalyst activity, polymer side chain branching, polymer M₂/M_w, polymer M_w/M_n, polymer density and polymer molecular weight of the resulting ethylene polymer by the addition of alkyl aluminum alkoxide in an amount to effect a final ratio of equivalents of aluminum to equivalents of chromium of from about 0.1:1 to about 10:1.

23. The process of claim 22 wherein said alkyl aluminum is triethyl aluminum, tri-isobutyl aluminum, or tri-n-hexyl aluminum.

24. The process of claim 22 wherein said alkyl aluminum alkoxide is diethyl aluminum ethoxide.

25. The process of claim 22, wherein said catalyst system further comprises titanium tetraisopropoxide.

26. The process of claim 22 wherein said polymerization is gas phase polymerization.

27. The process of claim 24 wherein said addition of diethyl aluminum ethoxide comprises in situ addition.

28. The process of claim 24 wherein said addition of diethyl aluminum ethoxide comprises addition directly to the catalyst during catalyst preparation.
29. The process of claim 22 wherein the polymer M_w/M_n is greater than or equal to 16 and the polymer M_z/M_w is greater than or equal to 6.
30. A process for producing an ethylene polymer comprising the steps of:
 - contacting ethylene under polymerization conditions with a catalyst system comprising silylchromate and a silica-containing support comprising silica selected from the group consisting of silica having:
 - (a) a pore volume of about 1.1 to about 1.8 cm^3/g and a surface area of about 245 to about 375 m^2/g ,
 - (b) a pore volume of about 2.4 to about 3.7 cm^3/g and a surface area of about 410 to about 620 m^2/g , and
 - (c) a pore volume of about 0.9 to about 1.4 cm^3/g and a surface area of about 390 to about 590 m^2/g ;
 - wherein said silica-containing support is dehydrated at about 400 to about 860°C;

and,

controlling catalyst productivity, reaction induction time and polymer molecular weight of the resulting ethylene polymer by the addition of an organoaluminum compound in an amount to effect a final ratio of equivalents of aluminum to equivalents of chromium of from about 0.1:1 to about 10:1.

31. The process of claim 30 wherein said addition of an organoaluminum compound comprises addition of diethyl aluminum ethoxide.
32. The process of claim 31 wherein said addition of diethyl aluminum ethoxide comprises in situ addition of diethyl aluminum ethoxide.

33. The process of claim 31 wherein said addition of said diethyl aluminum ethoxide comprises addition directly to the catalyst during catalyst preparation.
34. The process of claim 30 wherein said polymerization is gas phase polymerization.
35. The process of claim 30 wherein said silylchromate is loaded onto said silica-containing support at a loading of about 0.15 to about 1.0 weight percent of chromium.
36. The process of claim 30 wherein said addition of an organoaluminum compound comprises addition of an alkyl aluminum compound.
37. The process of claim 36 wherein said alkyl aluminum compound is selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum.
38. A process for producing an ethylene polymer comprising the steps of:

contacting ethylene under polymerization conditions with a catalyst system comprising silylchromate and a silica-containing support comprising silica selected from the group consisting of silica having:

(a) a pore volume of about 1.1 to about 1.8 cm³/g and a surface area of about 245 to about 375 m²/g, (b) a pore volume of about 2.4 to about 3.7 cm³/g and a surface area of about 410 to about 620 m²/g, and (c) a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g;

wherein said silica-containing support is dehydrated at about 400 to about 860°C;

and,

controlling catalyst activity, reaction induction time, and polymer molecular weight of the resulting ethylene polymer by the addition of a co-catalyst in an amount to effect a final ratio of equivalents of aluminum to equivalents of chromium of from about 0.1:1 to about 10:1.

39. The process of claim 38 wherein said step of contacting further comprises contacting with diethyl aluminum ethoxide.
40. The process of claim 38 wherein the co-catalyst is selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum.
41. The process of claim 38 wherein the ratio of equivalents of aluminum to equivalents of chromium is from about 1:1 to about 3:1.
42. The process of claim 38 wherein said polymerization is gas phase polymerization.
43. The process of claim 38 wherein said catalyst is treated, in-catalyst, with an alkyl aluminum or an alkyl aluminum alkoxide prior to said addition of co-catalyst.
44. The process of claim 43 wherein the alkyl aluminum alkoxide is diethyl aluminum ethoxide and the ratio of equivalents of aluminum to equivalents of chromium is between about 1:1 and about 10:1.
45. A process for producing an ethylene polymer comprising the steps of:
contacting ethylene under polymerization conditions with a catalyst system comprising chromium oxide and a silica-containing support comprising silica selected from the group consisting of silica having:
(a) a pore volume of about 1.1 to about 1.8 cm³/g and a surface area of about 245 to about 375 m²/g, (b) a pore volume of

about 2.4 to about 3.7 cm³/g and a surface area of about 410 to about 620 m²/g, and (c) a pore volume of about 0.9 to about 1.4 cm³/g and a surface area of about 390 to about 590 m²/g;

controlling catalyst activity, polymer M_w/M_n, and polymer molecular weight of the resulting ethylene polymer by the addition of a co-catalyst in an amount to effect a final ratio of equivalents of aluminum to equivalents of chromium of from about 0.1:1 to about 10:1.

46. The process of claim 45 wherein the co-catalyst is selected from the group consisting of triethyl aluminum, tri-isobutyl aluminum, and tri-n-hexyl aluminum.
47. The process of claim 45 wherein the ratio of equivalents of aluminum to equivalents of chromium is from about 1:1 to about 3:1.
48. The process of claim 45 wherein said polymerization is gas phase polymerization.
49. A process for producing an ethylene polymer in a reactor comprising contacting ethylene under polymerization conditions with a chrome catalyst system; conducting the polymerization at a space-time-yield value of greater than 8; and operating the polymerization at a catalyst productivity of greater than 3000 kg polymer/kg catalyst and at a reaction temperature at least 2.5°C higher than the reaction temperature when polymerizing with the same chrome catalyst system in the absence of triethyl aluminum and producing the ethylene polymer at the same polymer molecular weight and density using the same space-time-yield value, ethylene partial pressure, H₂/C₂ gas mole ratio and comonomer to C₂ gas mole ratio.
50. The process of claim 49, wherein the reactor is operated in condensing-mode.

51. The process of claim 49 or 50, wherein oxygen is added to modify the molecular weight or molecular weight distribution of the ethylene polymer after catalyst productivity and reaction temperature requirements are met.
52. The process of claim 49 wherein the chrome catalyst system comprising a silyl chromate catalyst systems or a chromium oxide catalyst system.
53. The process of claim 52 wherein the chrome catalyst system is a silyl chromate catalyst system.
54. The process of claim 52 wherein the chrome catalyst system is a chromium oxide catalyst system.
55. The process of claim 49 wherein the aluminum alkyl is diethylaluminum ethoxide.
56. The process of claim 49 or 50 wherein the polymerization at a space-time-yield value of greater than 8 is conducted in the presence of an aluminum alkyl added to the reactor separate from the chrome catalyst system.